



Photochemically triggered self-extraction of uranium from aqueous solution under ambient conditions

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ARTICLE INFO

Keywords:

Uranium
Photochemical
Extraction
Visible light
Seawater

ABSTRACT

Photocatalytic extraction of uranium from nuclear wastewater and seawater is a highly promising strategy to avoid environmental pollution and effectively recover uranium resources. Herein, we propose a novel strategy of photochemical for efficiently and high selectively extracting uranium from aqueous solution. The excited UO_2^{2+} at a suitable pH range were utilized for initiating the formation of hydrogen peroxide, which then directly reacted with UO_2^{2+} to form solid studtite ($\text{UO}_2\bullet 4\text{H}_2\text{O}$). This photochemically triggered extraction approach could remove $\sim 100.0\%$ of UO_2^{2+} from aqueous solution with U(VI) concentration of 10.0–200.0 ppm, and 62.7% of UO_2^{2+} from U(VI)-spiked real seawater after 24 hrs-irradiation under visible light even without additional electron-donor agents. The highly selective and high extraction efficiency towards uranium ranged in extremely wide concentrations demonstrated the powerful application potential in both the removal of uranium from nuclear wastewater and the extraction of uranium from seawater.

Data Availability: Data will be made available on request.

1. Introduction

Nuclear power energy has been considered as an ideal clean energy without the release of greenhouse gases, therefore the substitution of conventional fossil fuel energy with nuclear energy has been expected for a long time to some extent [1–5]. Uranium, which is regarded as the primary element for sustainably empowered nuclear reactors, is a necessary nuclear energy resource in urgent demand not only at present but also in the future [6–10]. However, with the rapid development of the nuclear power industry, radionuclide waste has threatened the survival of humans and caused environmental problems due to its natural radiological and chemical toxicity [11–14]. Meanwhile, in consideration of the strategic value of uranium and the limitation of uranium resources on land, exploring effective and highly selective strategies for uranium extraction from seawater and other uranium-containing wastewater from e.g. uranium mining and used fuel reprocessing and disposal is of great significance to the sustainable development of the nuclear industry [15–20]. Therefore, various technologies such as adsorption [21–30], electrochemical technology [31–37] and photocatalytic processes [38–47] have been explored to extract uranium from aqueous solution based on two aspects, i.e., environmental protection and resource utilization.

Among them, photocatalytic reduction of uranium has attracted extensive attention because it can effectively transform the soluble U(VI) into insoluble U(IV), facilitating subsequent separation from aqueous solution [5,42,48–50]. Over the past decades, plenty of various types of solid photocatalysts have been synthesized and further applied for the photoreduction of U(VI) from aqueous solutions, such as TiO_2 [50–53], $\text{g-C}_3\text{N}_4$ [54–58], MOFs [5,59–62] and COFs [48,63,64]. For examples, Li et al. proposed a strategy for capturing U(VI) from solution by a photocatalytic reduction process [38]. Under visible-light illumination, the photo-generated electrons from the photoactive MOF PCN-222 host modified with phosphorous and amino groups can effectively inhibit U(VI) pre-enriched inside MOF, resulting in neutral uranium-containing species which can evacuate the structure of MOF and regenerate the active sites rapidly for capturing additional U(VI). Yu et al. synthesized a UiO-66 -based heterostructured photocatalyst with spatially separated dual cocatalysts (MnO_x nanoparticles and $\text{Ti}_3\text{C}_2\text{T}_x$ MXene nanosheets) to achieve effective charge separation to remove U(VI), exhibiting excellent U(VI) extraction ability in varieties of U-containing wastewater and U(VI)-spiked real seawater [59]. Up to now, photocatalytic reduction alone or in conjunction with other technologies such as adsorption and chemical reduction has been proved able to efficiently extract uranium from aqueous solutions, but the employ of heterogeneous materials may

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<https://doi.org/10.1016/j.apcatb.2022.122092>

Received 1 September 2022; Received in revised form 1 October 2022; Accepted 20 October 2022

Available online 22 October 2022

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lead to further high-cost solid waste disposal with the potential risk of secondary pollution to the environment. Moreover, selectivity of uranium extraction is easily inhibited by the inevitable physical adsorption of coexisting ions on solid materials.

In 2021, our group reported an efficient strategy to selectively extract uranium from aqueous solution under visible-light irradiation in absence of solid photocatalyst [65]. With the excitation of U(VI) under visible light, U(VI) could be effectively extracted by forming brown uranium solid in the presence of alcohols at optimal pH value under anaerobic condition. However, the operation with inert gas was quite costly and inconvenient for application in industry. Herein, we developed a novel strategy for selectively extracting uranium as solid studtite ($\text{UO}_2(\text{O}_2) \cdot 4 \text{H}_2\text{O}$) under ambient conditions by employing the photochemical properties of U(VI) under visible light irradiation for thoroughly avoiding the usage of solid material and high-price inert gas. Especially, this aerobic uranium extraction method remains an excellent selectivity in seawater with the presence of complicated interfering substances such as alkali metal, transition metal and organics, which possesses a strong potential in practical application.

2. Experimental

2.1. Chemical and reagents

The U(VI) stock solution with concentration of $4201.68 \mu\text{mol/L}$ (1.0 g/L) was prepared by dissolving uranyl nitrate ($\text{UO}_2(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$, analytically pure, Beijing Research Institute of Chemical Engineering and Metallurgy, Beijing, China) into deionized water. In the bulk photochemical experiments, aqueous solutions with uranium concentration of $0\text{--}840.32 \mu\text{mol/L}$ ($0\text{--}200 \text{ mg/L}$) were all diluted from U(VI) stock solution. Other chemicals, including methanol (MeOH), ethanol (EtOH), isopropanol (IPA), benzyl alcohol (BA) were purchased from aladdin Chemical Reagent and used without any further purification.

2.2. Photochemical experiment

In a typical photochemical experiment, 42.5 mL of U(VI) solution with a wide concentration range from 0 to 200 mg/L was mixed with 7.5 mL MeOH (or other sacrificial agent) in a 100 mL reactor. The reactor was thermostated at 15°C with a cycling pump. The pH of the mixture was adjusted in the range of $2.0 \pm 0.1\text{--}7.0 \pm 0.1$ by adding negligible volumes of NaOH and HNO_3 solutions ($\sim 1.0 \text{ M}$). The suspension was magnetically stirred in dark for 1 h and then illuminated under visible light ($\lambda > 420 \text{ nm}$) using a 300 W Xe lamp (Microsolar 300, PerfectLight) equipped with a UV cutoff filter. At given intervals, aliquots (1.0 mL) of the suspension were pipetted and filtered through $0.22 \mu\text{m}$ membrane filter (Dismic-25, Advantec). The concentrations of UO_2^{2+} in solution were measured by using spectrophotometric method.

To further investigate the potential applications in uranium extraction from real seawater, the effects of competing ions such as K^+ , Ca^{2+} , Na^+ , Mg^{2+} , and Sr^{2+} ions on the selectivity of uranium extraction were studied. Furthermore, the real seawater ($\text{pH} = 8.37$) collected from Huanghai (Qingdao, China) was used. The concentrations of metal ions in the filtrate were measured by inductively coupled plasma optical emission spectrometer (ICP-OES, Horiba JY2000-2, Japan).

The details for characterization methods were presented in [Supporting Information](#).

3. Results and discussion

3.1. Enhanced photochemical extraction of U(VI)

In order to quantitatively evaluate the photochemical performance of uranium extraction, a series of uptake experiments were carried out. The removal efficiencies of U(VI) from the aqueous solution were examined under visible light irradiation at aerobic condition with

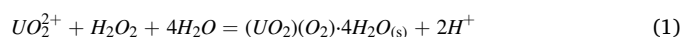
various pH values of $2.0\text{--}7.0$ (Fig. 1a). It is well known that U(VI) is prone to hydrolyze and precipitated in aqueous solution with high pH values, so the reaction at high pH has not been studied. The results showed that more than 86.7% of uranium can be extracted from the aqueous solution in the pH range of $4.0\text{--}6.0$ and 97.1% extraction efficiency of U(VI) can be achieved at pH 5.0 after 4 h irradiation. With the addition of the different concentrations of methanol as sacrificial agent, the results suggested that the extraction rate of uranium remarkably increased from 18.1% to 97.1% as the methanol concentration rose from 0 vol\% to 15 vol\% , and then remained at a high level until the concentration of methanol further increased to 80 vol\% (Fig. 1b). Notably, when the methanol amount was increased from 0% to 1% , the extraction percentage of U(VI) increased from 18.1% to 36.9% , indicating that methanol plays an important role during the photochemical process. In addition, other typical alcoholic sacrificial agents were used to replace methanol for photochemical extraction of U(VI) (Fig. 1c). The results showed that EtOH and IPA have the same excellent effect as methanol when used as sacrificial agents, but the removal efficiency of BA system was relatively low, which may be due to the low solubility of benzyl alcohol in water. Initial blank experiments in the absence of visible light irradiation showed that trace removal of U(VI) is observed, confirming that the extraction of uranium was driven by a photoreaction process (Fig. 1d). A controlled experiment in nitrogen (N_2) atmosphere also showed little removal of U(VI), while controlled experiments in both air and oxygen (O_2) atmosphere achieved high removal rate, confirming that the reaction pathway of U(VI) extraction under aerobic condition is different from that under inert atmosphere, and molecular oxygen plays an important role.

3.2. Characterization of the Photochemical-reaction Product

In the above reaction, we found that the original clear solution became turbid after 4 h of visible light irradiation. After filtration through Nylon membrane, light yellow solid powder was found on the membrane. The crystalline structure of the photochemical-reaction product was explored by XRD (Fig. 2a). The peaks at 15.067° , 15.174° , 21.102° , 26.314° and 30.403° corresponding to (200), (110), (-202), (310) and (400) planes matched with the standard patterns of studtite ($\text{UO}_2(\text{O}_2) \cdot 4 \text{H}_2\text{O}$) [66,67]. The spacing of 4.0 eV between the satellites and the main U $4f$ lines in XPS spectrum was in good agreement with the U(VI) in studtite reported in previous literature (Fig. 2b) [68]. FTIR spectrum of studtite was collected in the range of wave-number $4000\text{--}500 \text{ cm}^{-1}$ (Fig. S1). The broad adsorption peak appeared at 3472 and 3169 cm^{-1} are ascribed to the symmetric stretching vibration ($\nu(\text{OH})^{\text{sym}}$) and asymmetric stretching vibration of O-H-O ($\nu(\text{OH})^{\text{asym}}$), respectively. And the band at 1621 cm^{-1} is the bending vibration of H-O-H ($\delta(\text{HOH})$). Two typical bonds representing the U=O asymmetric stretching and symmetric stretching in the studtite are also seen at 906 and 726 cm^{-1} , respectively. In addition, the peaks centered at 602 cm^{-1} are assigned to the asymmetric stretching vibration of U-O ($\nu(\text{U-O}_{\text{peroxo}})^{\text{asym}}$) [66]. According to the SEM and TEM images (Fig. 2c-e), the obtained studtite was flower-shaped, composed of well-fined nanoflakes with the average diameter of $500\text{--}1000 \text{ nm}$. As expected, the elemental mapping (Fig. 2c) confirmed a homogenous distribution of U and O without any other elements. The crystalline features of studtite were also verified by HRTEM image (Fig. 2e), in which the (310) facet of studtite with interplanar distance of 0.338 nm was clearly found.

3.3. Formation of photochemical-reaction product

According to the literatures, studtite could be synthesized by the following reaction between uranyl and hydrogen peroxide (H_2O_2) [66]:



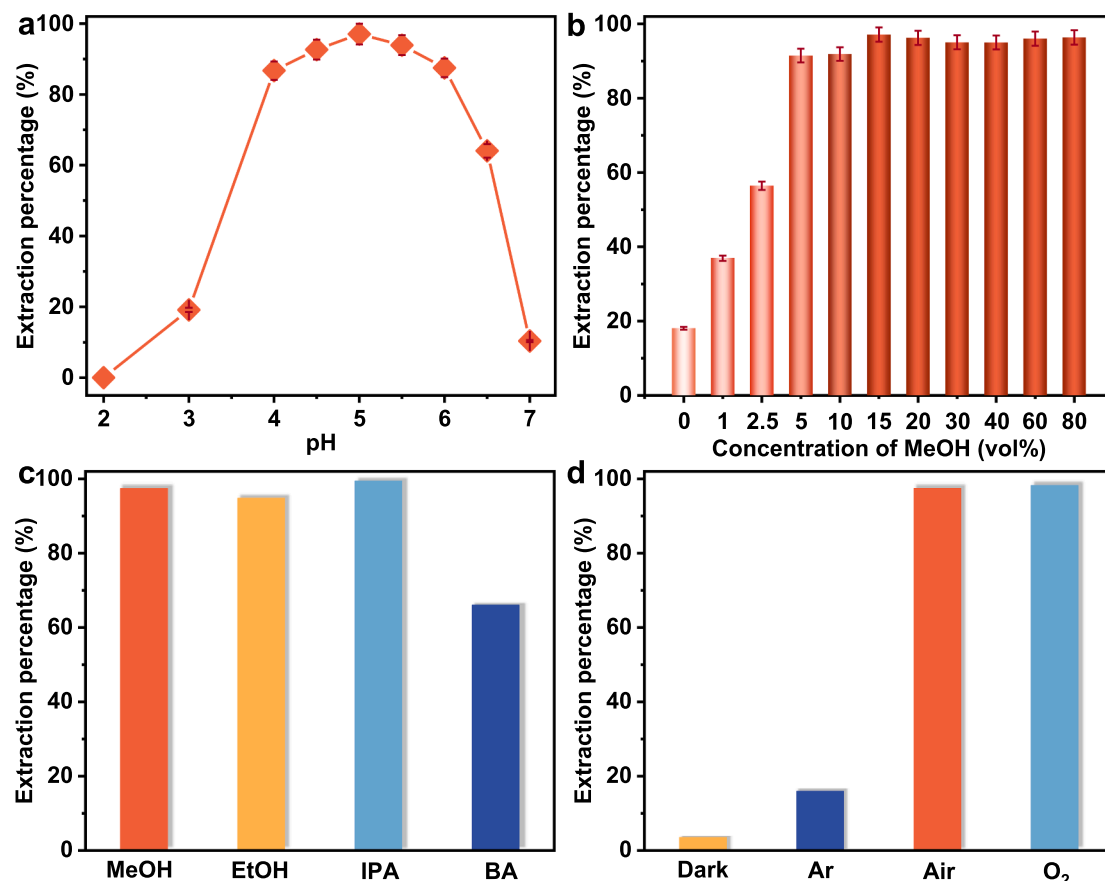


Fig. 1. (a) The pH effects on photochemical U(VI) extraction in air. $C_{U(VI)} = 50$ ppm, $C_{methanol} = 15$ vol%. (b) The effects of methanol concentration on photochemical U(VI) extraction in air. $C_{U(VI)} = 50$ ppm, pH = 5.0. (c) The effects of different alcohols as sacrificial agents on the photochemical extraction of U(VI) in air. $C_{U(VI)} = 50$ ppm, pH = 5.0, $C_{sacrificial\ agent} = 15$ vol%. (d) Control experiments for the photochemical extraction of U(VI) under different atmospheres. $C_{U(VI)} = 50$ ppm, pH = 5.0, $C_{methanol} = 15$ vol%. Reaction conditions: V = 5 mL, visible light ($\lambda > 420$ nm), 15 °C, and 4 h.

We tried to verify this reaction by adding a certain amount of hydrogen peroxide to the uranyl solution at pH 5.0 under dark condition. As expected, solid stutite was formed successfully (Figs. S2 and S3). Therefore, we then investigated the generation of H_2O_2 during photochemical reaction. No significant H_2O_2 generation was observed in the dark. While considerable H_2O_2 was detected with the addition of visible light, which proved the formation of H_2O_2 during the photoreaction and that stutite precipitation was formed by the reaction between H_2O_2 and UO_2^{2+} . Under different pH conditions, the amount of detected H_2O_2 during the reaction process was different (Fig. 3a). At pH 4.0 or 4.5, H_2O_2 was generated continuously with the extension of illumination time, while at pH 5.0, 5.5 or 6.0, the amount of H_2O_2 increased first and then decreased with the increasing illumination time. According to Eq. (1), the formation of stutite will be inhibited under acidic conditions, which would result in continuous accumulation of H_2O_2 and reduced extraction efficiencies of U(VI) at pH 4 and 4.5 (Fig. 3a-b). Since H_2O_2 hydrolysis will be accelerated under alkaline conditions [69], the detected H_2O_2 amount is low and the formation of stutite is slow at pH 6 (Fig. 3a-b). Therefore, the formation of stutite could be optimal at appropriate pH (pH 5.0). To further evaluate the extraction capacity of this photochemical approach, the initial uranium concentration-dependent removal kinetics was examined at pH 5.0. As shown in Fig. 3d, all concentrations of U(VI) solution can be solidified into stutite after 18 h photochemical reaction, proving the feasibility of this photochemical approach in low-concentration uranium-containing seawater. The reaction rate was increased with the increase of $C_0(U)$ from 10 to 200 ppm. Meanwhile, H_2O_2 generation also increased with increasing initial uranium concentration, reaching 0.26, 0.37, 0.39, 0.57

and 0.59 mM H_2O_2 for the respective initial uranium concentrations of 10, 20, 50, 100 and 200 ppm, after irradiation under visible light for 24 h (Fig. 3c). It is noteworthy that H_2O_2 showed a sharp consumption at the initial stage of the reaction with the high initial concentration of U(VI). However, the detected H_2O_2 showed a trend of slow accumulation as the concentration of U(VI) decreased and the corresponding U(VI) removal rate was also relatively low (Fig. 3d). These results further proved that the extraction performance of U(VI) was connected with the produced H_2O_2 , which was dependent on the initial U(VI) concentration and was promoted with high concentration of U(VI).

From the above experimental results, it can be found that in this photo-reaction system, UO_2^{2+} reacts directly with hydrogen peroxide to produce stutite with four crystalline waters, which is not consistent with the results in some literatures, so we further explored the factors affecting the crystalline water of uranium peroxide [38,59,70]. When adjusting the reaction temperature, it was found that the photochemical reaction products collected at different reaction temperatures were different (Fig. 4a). With the reaction temperature rose to higher than 60 °C, the product was completely transformed from stutite ($(UO_2)(O_2) \cdot 4 H_2O$) to metastutite ($(UO_2)(O_2) \cdot 2 H_2O$), which was caused by the removal of two crystalline waters in the product at high temperature [71]. The initial removal rate of UO_2^{2+} was increased with the increasing temperature, but the final extraction percentage (after 12 hrs irradiation) was decreased with the increasing temperature (Fig. 4b). In combination with the detected H_2O_2 amount at different intervals, it could be implied that at higher temperature the accumulated amount of hydrogen peroxide in the system was dramatically reduced, which might be caused by the decomposition of H_2O_2 under higher temperature

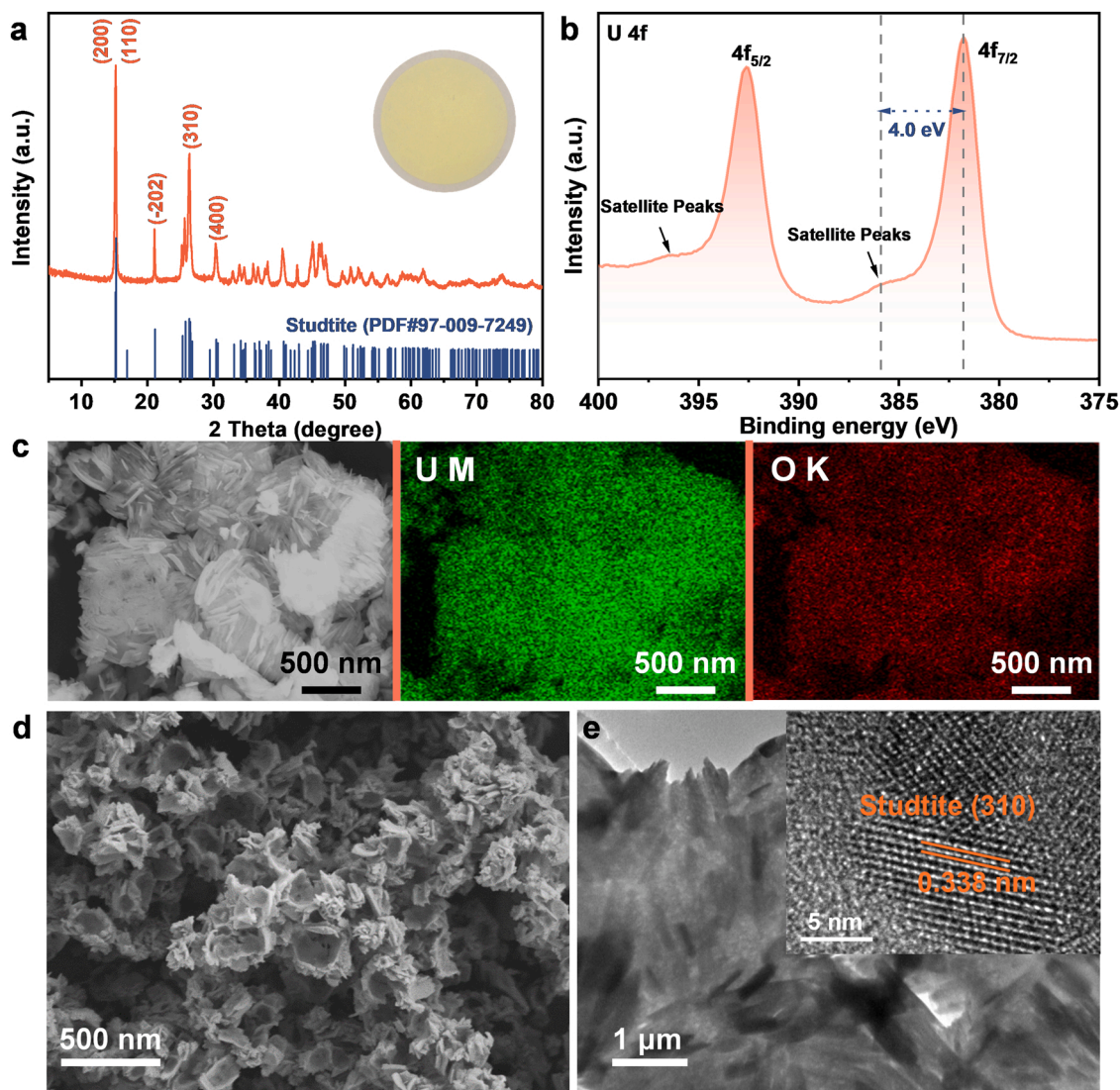


Fig. 2. (a) XRD patterns of generated studtite at 15 °C. Insert: image of the generated studtite after photochemical reaction. (b) High-resolution XP spectra of U 4f of generated studtite. (c) Elemental mapping images of generated studtite. (d) SEM image of generated studtite. (e) TEM image of generated studtite. Insert: HRTEM image of generated studtite.

(Fig. 4c).

3.4. Mechanism of uranium extraction in the photochemical system

The UV-Vis adsorption spectra of U(VI)/methanol mixture at various concentrations of methanol at pH 5.0 shown in Fig. 5a exhibited an absorption band around 425 nm, which was due to electron transition from O_{2p} to an empty 5f-orbital of the central U atom [72]. The significant increase in the absorption with the addition of methanol was observed and a red shift of the absorption maxima for methanol/U(VI) mixture (with 60% and 80% methanol) compared to the uranyl solution was also detected, indicating the formation of a complex between the uranyl ion and methanol at high concentration of methanol [73,74]. Furthermore, the corresponding photoluminescence (PL) spectra showed a very broad peak ranging from 450 to 650 nm with maximum at 525 nm for U(VI) solution (Fig. 5b) [72]. The intensity decreased sharply with the addition of methanol and gradually decreased with the increasing methanol concentration, revealing that quenching of photo-excited $^*UO_2^{2+}$ by methanol, which is in line with the boosted photochemical extraction of U(VI) in the case of alcohols as sacrificial agent [53,75]. Figs. 5c and S4 illustrated the UV-Vis absorption spectra of U(VI)

solution in the case of with and without methanol at different pH values. It should be noted that visible light absorption band for U(VI) solution appeared when pH is higher than 4.0, and then enhanced as the pH value increased from 4.0 to 7.0. After adding 15% methanol into the U(VI) solution, the spectra of the U(VI)/methanol mixture at varying pH values displayed the same trends as that of U(VI) solution, which explained the reason for the low extraction efficiency at low pH in Fig. 1a. However, the PL spectra of U(VI) solution at various pH in the case of with and without methanol were different. The emission intensity maximum of U(VI) solution was centered at 525 nm and increased significantly with pH in the range 2.0–6.5, but decreased at pH 7.0 (Fig. S5). While for U(VI)/methanol mixture, the emission intensity promoted with pH increasing from 2.0 to 7.0, and the emission intensity maxima was blue-shifted at pH 7.0 (Fig. 5d). In brief, UO_2^{2+} could be excited to $^*UO_2^{2+}$ by absorbing visible light at appropriate pH, and the addition of sacrificial agent such as methanol promoted the separation of photogenerated carriers, thus speeding up the photochemical extraction process of uranium.

Based on above discussion, the removal of uranium originated from the formation of solid studtite, which was generated by the reaction between produced H_2O_2 and U(VI) at appropriate pH value, so it's

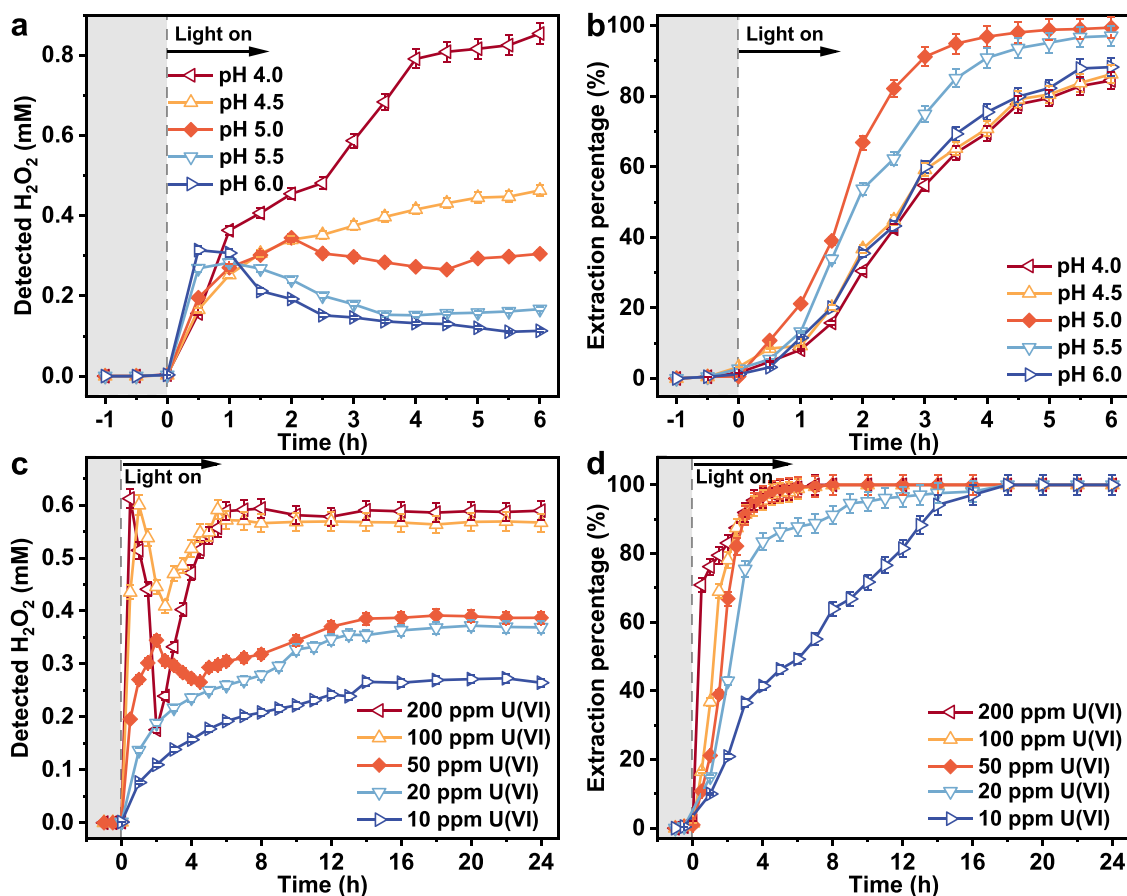


Fig. 3. (a) The pH effects on generation of H_2O_2 during photochemical reaction. $C_{U(VI)} = 50$ ppm, $C_{methanol} = 15$ vol%. (b) The pH effects on the photochemical extraction of U(VI). $C_{U(VI)} = 50$ ppm, $C_{methanol} = 15$ vol%. (c) The effects of U(VI) concentrations on generation of H_2O_2 during photochemical reaction. pH = 5.0, $C_{methanol} = 15$ vol%. (d) The effects of U(VI) concentrations on the photochemical extraction of U(VI). pH = 5.0, $C_{methanol} = 15$ vol%. Reaction conditions: V = 50 mL, air, visible light ($\lambda > 420$ nm), 15 °C.

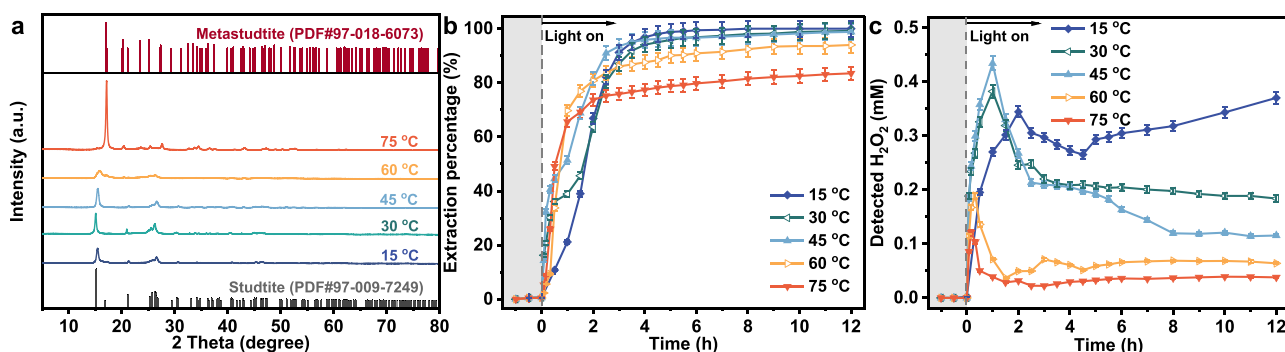


Fig. 4. (a) XRD patterns of generated solid at different reaction temperature. (b) The effects of reaction temperature on the photochemical extraction of U(VI). (c) The effects of reaction temperature on generation of H_2O_2 during photochemical reaction. Reaction conditions: $C_{U(VI)} = 50$ ppm, pH = 5.0, $C_{methanol} = 15$ vol%, air, visible light ($\lambda > 420$ nm).

needed to figure out how H_2O_2 was generated during the photochemical process. The production of reactive intermediate species under visible-light illumination was investigated by electron paramagnetic resonance (EPR). The EPR spectrum exhibited a typical four-splitting pattern in Fig. 6a with relative intensities of 1:2:2:1, suggesting the formation of DMPO/ $\bullet OH$ radical adducts [76]. Apparently, the signal intensity of DMPO/ $\bullet OH$ radical adducts was significantly reduced in the presence of methanol, while an additional signal assigned to the DMPO/Carbon-centered ($\bullet C$) radical adduct with relative intensities of 1:1:1:1:1 was obtained (Fig. 6b) [77,78]. The results implied that the

U(VI) solution at pH value of 5.0 could generate hydroxyl radicals when excited under visible light. After adding methanol, efficient separation of photogenerated carriers could be achieved due to the consuming of the photogenerated holes and hydroxyl radicals. Therefore, the formation of H_2O_2 could be formed via two pathways: one is via two-electrons oxygen reduction [79], the other is based on hydroxyl radical recombination [80].

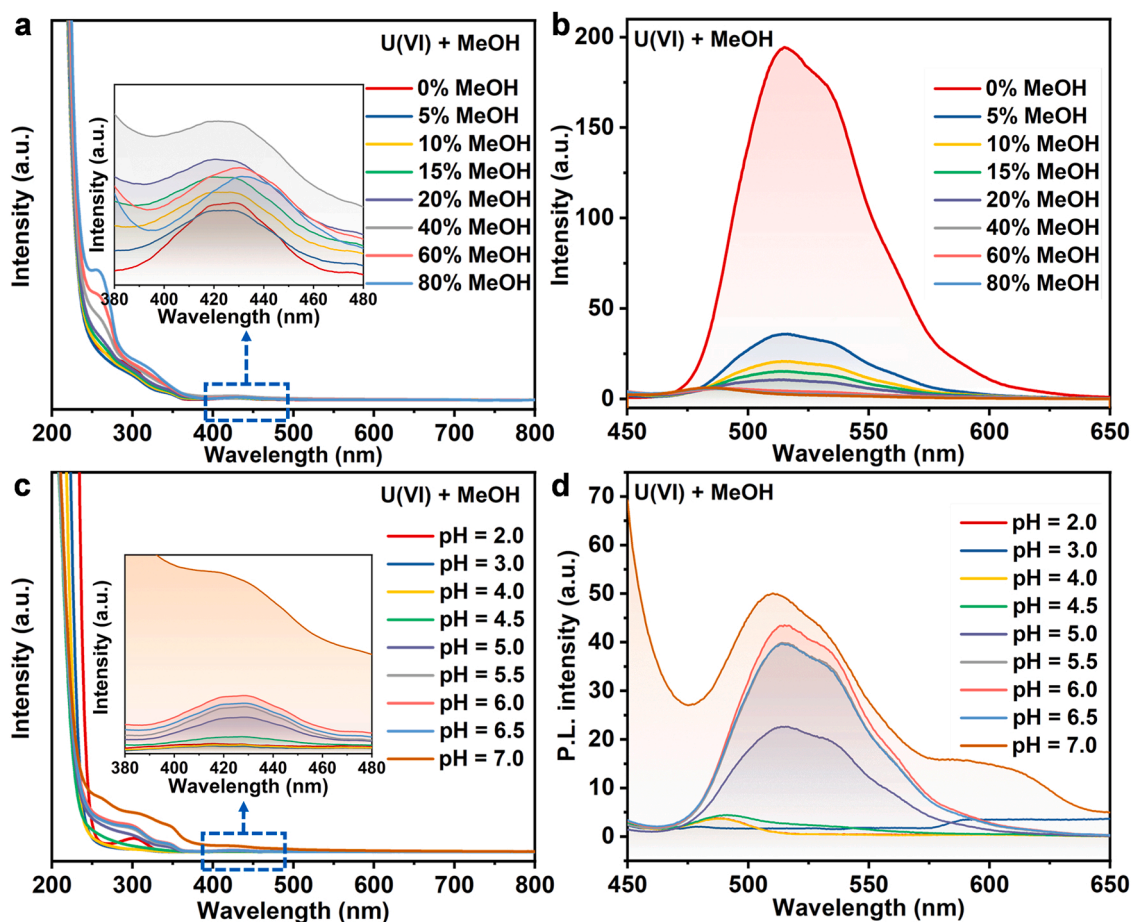


Fig. 5. (a) The effects of methanol concentrations on UV-Vis absorption spectra of U(VI)/Methanol mixture. $C_{U(VI)} = 50$ ppm. Insert: magnified spectra from 380 to 480 nm. (b) The effects of methanol concentrations on photoluminescence spectra of U(VI)/Methanol mixture. $C_{U(VI)} = 50$ ppm, $\lambda_{ex} = 420$ nm. (c) The effects of pH on UV-Vis absorption spectra of U(VI)/Methanol mixture. $C_{U(VI)} = 50$ ppm, $C_{methanol} = 15$ vol%. (d) The effects of pH on photoluminescence spectra of U(VI)/Methanol mixture. $C_{U(VI)} = 50$ ppm, $C_{methanol} = 15$ vol%, $\lambda_{ex} = 420$ nm.

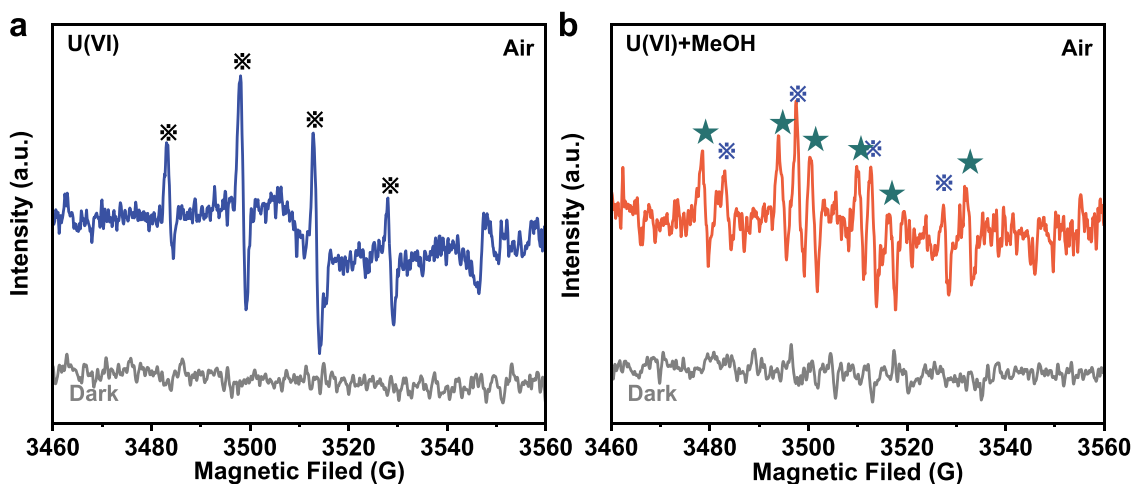


Fig. 6. (a) EPR spectra collected from U(VI) solution with DMPO in air under dark and visible light irradiation. (b) EPR spectra collected from U(VI)/Methanol mixture with DMPO in air under dark and visible light irradiation.

3.5. Extraction of uranium without extra sacrificial agent

Through the EPR results, we found that $\bullet OH$ radical existed in the system without methanol as the sacrificial agent. We further analyzed the source of hydroxyl radical in the system. In the absence of methanol,

UO_2^{2+} could still be extracted at appropriate pH under visible light irradiation, but the extraction time was relatively long since the production of hydrogen peroxide was slow. At the optimum pH 6.0, the UO_2^{2+} extraction rate reached 94.8% after 120 h of visible light irradiation (Fig. 7a). We further checked the presence of H_2O_2 under Ar

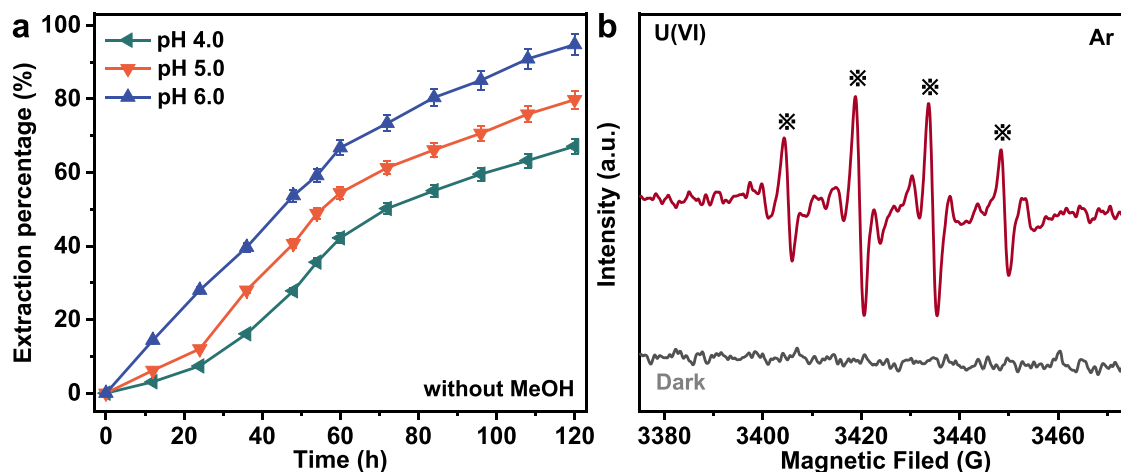


Fig. 7. (a) The pH effects on photochemical extraction of U(VI) in the absence of MeOH. Reaction conditions: $C_{U(VI)} = 50$ ppm, air, visible light ($\lambda > 420$ nm), 15°C . (b) EPR spectra of U(VI) solution with the addition of DMPO in Ar atmosphere under dark /visible-light irradiation.

atmosphere to reveal whether hydroxyl radicals were from the oxidation of water by photogenerated holes or from the transformation of reactive oxygen species. It is worth noting that H_2O_2 can be produced even in Ar atmosphere (Fig. S6). Combined with the in situ EPR test under Ar atmosphere (Fig. 7b), it was proved that the photogenerated holes generated by the excited of UO_2^{2+} with visible light irradiation have the ability to oxidize water into $\cdot\text{OH}$ radical, which is further coupled to produce H_2O_2 .

From above analysis, a possible mechanism of photochemical extraction of U(VI) was proposed as Scheme 1. Firstly, UO_2^{2+} could absorb visible light to produce an excited state $^*\text{UO}_2^{2+}$ at optimal pH value, then $^*\text{UO}_2^{2+}$ was further converted to UO_2^+ in the presence of water or organics such as alcohols, meanwhile hydroxyl radical and/or carbon radical was produced. In the case of sufficient oxygen, U(V) avoided the disproportionation reaction to form U(IV), but transferred into UO_2^{2+} , with H_2O_2 formation from the oxygen reduction and the combination of hydroxyl radicals. The resulting H_2O_2 then reacted directly with the UO_2^{2+} to yield the light yellow solid studtite (UO_2) $\text{O}_2 \cdot 4\text{H}_2\text{O}$, so as to realize uranium extraction from aqueous solution in the presence or absence of extra electron donor.

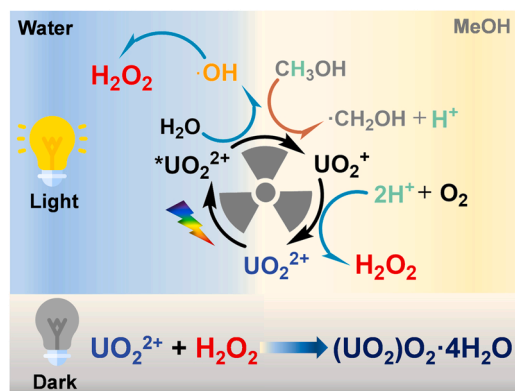
3.6. Selective uranium extraction and its application in seawater

Considering uranium mining and milling as well as nuclear accidents would contaminate portable water sources, rivers, and oceans with abundant of co-existing metal ions, the influence of K^+ , Na^+ , Ca^{2+} , Mg^{2+} to the extraction performance of U(VI) as function of initial M/U ratio

from 10 to 10,000 were further investigated to examine the feasibility of selective uranium extraction from complicated solution matrix. As shown in Fig. 8a, the extraction percentage of U(VI) reduced at different M/U ratios, but still remained at around 70.0% after 24 h irradiation. The extraction percentage of U(VI) from solution containing multiple interfering ions including Sr^{2+} , K^+ , Na^+ , Ca^{2+} and Mg^{2+} shows a slightly decrease compared with the case without interfering ions, but the selectivity for uranium extraction was still excellent even though the concentration of uranyl ion is only 1 ppm which is 1/1000 of the interfering cations (Fig. 8b). In order to examine the applicability of this photochemical approach for extraction of uranyl in complicated ocean environment, we further investigated the extraction efficiency of U(VI) in real seawater (collected from the East China Sea, pH = 8.37). With pH 5, 62.7% of initial ~ 1 ppm U(VI) in the seawater can be extracted after 24 hrs-photoreaction in the absence of extra electron donor agent, which implied the possibility of applying this technology for effective uranium extraction from seawater.

4. Conclusion

In summary, we have proposed an efficient and selective visible light-triggered uranium extraction technology from wastewater and seawater without solid materials. By optimizing the pH range of uranium solution and the concentration of electron donor, U(VI) can be efficiently extracted through the direct reaction between UO_2^{2+} and H_2O_2 generated from the U(VI) species-triggered photo-reaction, forming studtite and separating from aqueous solution. 100.0% of UO_2^{2+} can be removed from aqueous solutions at concentrations ranging from 10.0 ppm to 200.0 ppm in the presence of 15 vol% methanol at pH 5.0 with this photochemically triggered extraction method. Even in the absence of extra electron donor, the effective removal of uranyl can be achieved by appropriately prolonging the reaction time. Moreover, results suggest that interfering cations such as Sr^{2+} , K^+ , Na^+ , Ca^{2+} and Mg^{2+} , have no competing effect for the selective uranium extraction. 62.7% of initial ~ 1 ppm U(VI) in the seawater can be extracted after 24 hrs-photoreaction in the absence of extra electron donor agent, confirming the promising application prospect of the proposed photochemically triggered self-extraction strategy. In brief, without involving of any solid materials, and only visible light as extra energy input, uranium was found to be extracted selectively in form of studtite in the presence or even in the absence of extra electron donor under ambient conditions. Our current work identifies promising opportunities for the economical and efficient extraction of uranium from oceans and other uranium-containing water.



Scheme 1. The proposed schematic mechanism of U(VI) photochemical extraction.

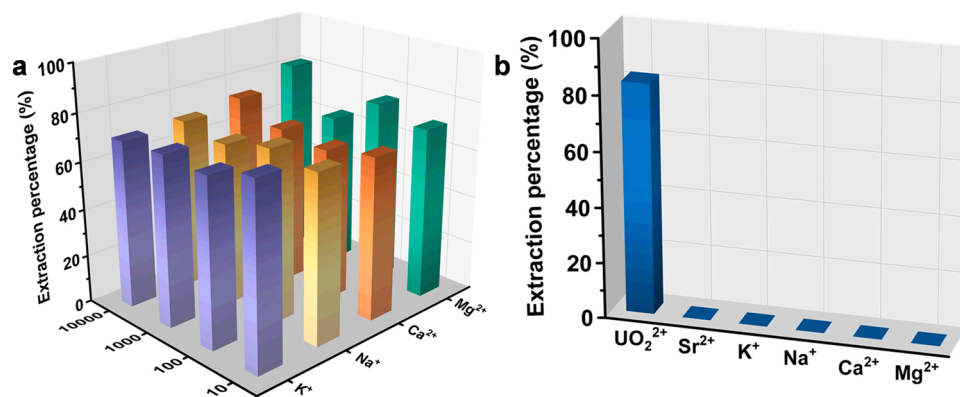


Fig. 8. The effects of different ratios of alkali metal to U(VI) on the photochemical extraction of U(VI). $C_{U(VI)} = 1$ ppm, pH = 5.0, $C_{\text{methanol}} = 15$ vol%. (b) The extraction percentage of metal ion in the presence of multiple interfering anions. $C_{U(VI)} = 1$ ppm, pH = 5.0, $C_{\text{methanol}} = 15$ vol%, $C_{(\text{Sr}, \text{K}, \text{Na}, \text{Ca}, \text{Mg ion})} = 1000$ ppm. Reaction conditions: air, visible light ($\lambda > 400$ nm), 15 °C, and 24 h.

CRedit authorship contribution statement

Yezi Hu: Conceptualization, Investigation, Experiments, Data analysis, Writing – original draft. **Duoyue Tang:** Validation, Data analysis. **Zewen Shen:** Validation, Data analysis. **Ling Yao:** Data analysis. **Guixia Zhao:** Supervision, Conceptualization, Writing – review & editing, Funding acquisition. **Xiangke Wang:** Resources, Funding acquisition, Supervision, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgments

We sincerely acknowledge the financial supports by the National Key Research and Development Program of China (2018YFC1900105), NSFC (21976054, 22176054), Science Challenge Project (TZ2016004) and Beijing Outstanding Young Scientist Program.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.apcatb.2022.122092](https://doi.org/10.1016/j.apcatb.2022.122092).

References

- [1] Y.F. Yue, R.T. Mayes, J. Kim, P.F. Fulvio, X.G. Sun, C. Tsouris, J. Chen, S. Brown, S. Dai, Seawater uranium sorbents: preparation from a mesoporous copolymer initiator by atom-transfer radical polymerization, *Angew. Chem. Int. Ed. Engl.* 52 (2013) 13458–13462.
- [2] Y. Lu, Uranium extraction: coordination chemistry in the ocean, *Nat. Chem.* 6 (2014) 175–177.
- [3] Q. Sun, B. Aguila, J. Perman, A.S. Ivanov, V.S. Bryantsev, L.D. Earl, C.W. Abney, L. Wojtas, S. Ma, Bio-inspired nano-traps for uranium extraction from seawater and recovery from nuclear waste, *Nat. Commun.* 9 (2018) 1644.
- [4] B. Aguila, Q. Sun, H. Cassidy, C.W. Abney, B. Li, S. Ma, Design strategies to enhance amidoxime chelators for uranium recovery, *ACS Appl. Mater. Interfaces* 11 (2019) 30919–30926.
- [5] H.L. Zhang, W. Liu, A. Li, D. Zhang, X.Y. Li, F.W. Zhai, L.H. Chen, L. Chen, Y. L. Wang, S.A. Wang, Three mechanisms in one material: uranium capture by a polyoxometalate-organic framework through combined complexation, chemical reduction, and photocatalytic reduction, *Angew. Chem. Int. Ed. Engl.* 58 (2019) 16110–16114.
- [6] W. Wongjakkham, D. Wongsawaeng, P. Hosemann, C. Kanokworakan, V. Ratnitsai, Enhancement of uranium recovery from seawater using amidoximated polymer gel synthesized from radiation-polymerization and crosslinking of acrylonitrile and methacrylic acid monomers, *J. Environ. Chem. Eng.* 6 (2018) 2768–2777.
- [7] F.F. Zhang, H.S. Zhang, R.R. Chen, Q. Liu, J.Y. Liu, C. Wang, Z.Y. Sun, J. Wang, Mussel-inspired antifouling magnetic activated carbon for uranium recovery from simulated seawater, *J. Colloid Interface Sci.* 534 (2019) 172–182.
- [8] N. Tang, J. Liang, C.G. Niu, H. Wang, Y. Luo, W.L. Xing, S.J. Ye, C. Liang, H. Guo, J. Y. Guo, Y.F. Zhang, G.M. Zeng, Amidoxime-based materials for uranium recovery and removal, *J. Mater. Chem. A* 8 (2020) 7588–7625.
- [9] M. Ahmad, J.J. Chen, K. Yang, T. Shah, M.-u-d Naik, Q.Y. Zhang, B.L. Zhang, Preparation of amidoxime modified porous organic polymer flowers for selective uranium recovery from seawater, *Chem. Eng. J.* 418 (2021), 129370.
- [10] W.R. Cui, C.R. Zhang, R.H. Xu, X.R. Chen, R.H. Yan, W. Jiang, R.P. Liang, J.D. Qiu, Low Band Gap Benzoxazole-Linked Covalent Organic Frameworks for Photo-Enhanced Targeted Uranium Recovery, *Small* 17 (2021), e2006882.
- [11] T. Chen, J. Zhang, M.X. Li, H.L. Ge, Y. Li, T. Duan, W.K. Zhu, Biomass-derived composite aerogels with novel structure for removal/recovery of uranium from simulated radioactive wastewater, *Nanotechnology* 30 (2019), 455602.
- [12] L.J. Kong, Y. Ruan, Q.Y. Zheng, M.H. Su, Z.H. Diao, D.Y. Chen, L.A. Hou, X. Y. Chang, K.M. Shih, Uranium extraction using hydroxyapatite recovered from phosphorus containing wastewater, *J. Hazard. Mater.* 382 (2020), 120784.
- [13] F.F. Li, W.R. Cui, W. Jiang, C.R. Zhang, R.P. Liang, J.D. Qiu, Stable sp² carbon-conjugated covalent organic framework for detection and efficient adsorption of uranium from radioactive wastewater, *J. Hazard. Mater.* 392 (2020), 122333.
- [14] J. Liao, T. Xiong, L. Ding, Y. Zhang, W.K. Zhu, Effective separation of uranium(VI) from wastewater using a magnetic carbon as a recyclable adsorbent, *Sep. Purif. Technol.* 282 (2022), 120140.
- [15] C. Tsouris, Uranium extraction: Fuel from seawater, *Nat. Energy* 2 (2017) 17022.
- [16] B.F. Parker, Z. Zhang, L. Rao, J. Arnold, An overview and recent progress in the chemistry of uranium extraction from seawater, *Dalton Trans.* 47 (2018) 639–644.
- [17] H.Y. Wu, F.T. Chi, S. Zhang, J. Wen, J. Xiong, S. Hu, Control of pore chemistry in metal-organic frameworks for selective uranium extraction from seawater, *Micro Mesopor. Mater.* 288 (2019), 109567.
- [18] Z.Y. Wang, Q.H. Meng, R.C. Ma, Z.K. Wang, Y.J. Yang, H.Y. Sha, X.J. Ma, X. H. Ruan, X.Q. Zou, Y. Yuan, G.S. Zhu, Constructing an Ion Pathway for Uranium Extraction from Seawater, *Chem* 6 (2020) 1683–1691.
- [19] H. Li, S.A. Wang, Reaction: semiconducting MOFs offer new strategy for uranium extraction from seawater, *Chem* 7 (2021) 279–280.
- [20] S.X. Wen, Y. Sun, R.R. Liu, L. Chen, J.W. Wang, S.Y. Peng, C.X. Ma, Y.H. Yuan, W. T. Gong, N. Wang, Supramolecular Poly(amidoxime)-Loaded Macroporous Resin for Fast Uranium Recovery from Seawater and Uranium-Containing Wastewater, *ACS Appl. Mater. Interfaces* 13 (2021) 3246–3258.
- [21] G. Cheng, A.R. Zhang, Z.W. Zhao, Z.M. Chai, B.W. Hu, B. Han, Y.J. Ai, X.K. Wang, Extremely stable amidoxime functionalized covalent organic frameworks for uranium extraction from seawater with high efficiency and selectivity, *Sci. Bull.* 66 (2021) 1994–2001.
- [22] L.J. Feng, H. Wang, T.T. Feng, B.J. Yan, Q.H. Yu, J.C. Zhang, Z.H. Guo, Y.Y. Yuan, C.X. Ma, T. Liu, N. Wang, In-situ synthesis of uranyl-imprinted nanocage for selective uranium recovery from seawater, *Angew. Chem. Int. Ed. Engl.* 134 (2021) 82–86.
- [23] H.Q. Gu, P.H. Ju, Q. Liu, G.H. Sun, J.Y. Liu, R.R. Chen, J. Yu, J.H. Zhu, J. Wang, Constructing an Amino-reinforced amidoxime swelling layer on a Polyacrylonitrile surface for enhanced uranium adsorption from seawater, *J. Colloid Interface Sci.* 610 (2021) 1015–1026.
- [24] S.C. Liu, M.B. Wu, H. Ye, L. Liu, L.L. Ma, J. Yao, Amidoximated cellulose microspheres synthesized via homogenous reactions for High-Performance extraction of uranium from seawater, *Chem. Eng. J.* 426 (2021), 131378.
- [25] C.Z. Wang, Z.F. Chai, W.Q. Shi, Ultrahigh affinity and selectivity nanotaps for uranium extraction from seawater, *ACS Cent. Sci.* 7 (2021) 1602–1604.

- [26] Y. Wang, Z.W. Lin, Q. Liu, J.H. Zhu, J.Y. Liu, J. Yu, R.R. Chen, P.L. Liu, J. Wang, Simple one-step synthesis of woven amidoximated natural material bamboo strips for uranium extraction from seawater, *Chem. Eng. J.* 425 (2021), 131538.
- [27] Y. Wang, Z.W. Lin, J.H. Zhu, J.Y. Liu, J. Yu, R.R. Chen, P.L. Liu, Q. Liu, J. Wang, Ultra-high flexibility amidoximated ethylene acrylic acid copolymer film synthesized by the mixed melting method for uranium adsorption from simulated seawater, *J. Hazard. Mater.* (2021), 127808.
- [28] Z.X. Liu, Z.Y. Xu, L.F. Xu, F. Buyong, T.C. Chay, Z. Li, Y.W. Cai, B.W. Hu, Y.L. Zhu, X.K. Wang, Modified biochar: synthesis and mechanism for removal of environmental heavy metals, *Carbon Res.* 1 (2022) 8.
- [29] H.B. Chen, Y.R. Gao, J.H. Li, Z. Fang, N. Bolan, A. Bhatnagar, B. Gao, D.Y. Hou, S. S. Wang, H. Song, X. Yang, S.M. Shaheen, J. Meng, W.F. Chen, J. Rinklebe, H. L. Wang, Engineered biochar for environmental decontamination in aquatic and soil systems: a review, *Carbon Res.* 1 (2022) 4.
- [30] M. Hao, X. Liu, X. Liu, J. Zhang, H. Yang, G.I.N. Waterhouse, X. Wang, S. Ma, Converging cooperative functions into the nanospace of covalent organic frameworks for efficient uranium extraction from seawater, *CCS Chem.* 4 (2022) 2294–2307.
- [31] C. Liu, P.C. Hsu, J. Xie, J. Zhao, T. Wu, H.T. Wang, W. Liu, J.S. Zhang, S. Chu, Y. Cui, A half-wave rectified alternating current electrochemical method for uranium extraction from seawater, *Nat. Energy* 2 (2017) 17007.
- [32] F.T. Chi, S. Zhang, J. Wen, J. Xiong, S. Hu, Highly Efficient Recovery of Uranium from Seawater Using an Electrochemical Approach, *Ind. Eng. Chem. Res.* 57 (2018) 8078–8084.
- [33] T. Liu, J.L. Yuan, B. Zhang, W.B. Liu, L.M. Lin, Y. Meng, S.F. Yin, C.B. Liu, F. B. Luan, Removal and recovery of uranium from groundwater using direct electrochemical reduction method: performance and implications, *Environ. Sci. Technol.* 53 (2019) 14612–14619.
- [34] P.P. Zhang, L. Wang, Z.W. Huang, J.P. Yu, Z.J. Li, H. Deng, T.Q. Yin, L. Yuan, J. K. Gibson, L. Mei, L.R. Zheng, H.Q. Wang, Z.F. Chai, W.Q. Shi, Aryl Diazonium-Assisted Amidoximation of MXene for Boosting Water Stability and Uranyl Sequestration via Electrochemical Sorption, *ACS Appl. Mater. Interfaces* 12 (2020) 15579–15587.
- [35] H. Yang, X.L. Liu, M.J. Hao, Y.H. Xie, X.K. Wang, H. Tian, G.I.N. Waterhouse, P. E. Kruger, S.G. Telfer, S.Q. Ma, Functionalized Iron-Nitrogen-Carbon Electrocatalyst Provides a Reversible Electron Transfer Platform for Efficient Uranium Extraction from Seawater, *Adv. Mater.* 33 (2021), e2106621.
- [36] X. Liu, Y. Xie, M. Hao, Z. Chen, H. Yang, G.I.N. Waterhouse, S. Ma, X. Wang, Highly Efficient Electrocatalytic Uranium Extraction from Seawater over an Amidoxime-Functionalized In–N–C Catalyst, *Adv. Sci.* 9 (2022), 2201735.
- [37] Y. Cai, Y. Zhang, Z. Lv, S. Zhang, F. Gao, M. Fang, M. Kong, P. Liu, X. Tan, B. Hu, X. Wang, Highly Efficient Uranium Extraction by a Piezo Catalytic Reduction-Oxidation Process, *Appl. Catal. B: Environ.* 310 (2022), 121343.
- [38] H. Li, F.W. Zhai, D.X. Gui, X.X. Wang, C.F. Wu, D. Zhang, X. Dai, H. Deng, X.T. Su, J. Diwu, Z. Lin, Z.F. Chai, S.A. Wang, Powerful uranium extraction strategy with combined ligand complexation and photocatalytic reduction by postsynthetically modified photoactive metal-organic frameworks, *Appl. Catal. B: Environ.* 254 (2019) 47–54.
- [39] W.R. Cui, F.F. Li, R.H. Xu, C.R. Zhang, X.R. Chen, R.H. Yan, R.P. Liang, J.D. Qiu, Regenerable Covalent Organic Frameworks for Photo-enhanced Uranium Adsorption from Seawater, *Angew. Chem. Int. Ed. Engl.* 59 (2020) 17684–17690.
- [40] Y.Y. Yuan, B.Y. Niu, Q.H. Yu, X. Guo, Z.H. Guo, J. Wen, T. Liu, H.Q. Zhang, N. Wang, Photoinduced Multiple Effects to Enhance Uranium Extraction from Natural Seawater by Black Phosphorus Nanosheets, *Angew. Chem. Int. Ed. Engl.* 59 (2020) 1220–1227.
- [41] B. Chen, G.K. Zhang, L. Chen, J.Y. Kang, Y.H. Wang, S.Y. Chen, Y.D. Jin, H.J. Yan, C.Q. Xia, Visible light driven photocatalytic removal of uranium(VI) in strongly acidic solution, *J. Hazard. Mater.* (2021), 127851.
- [42] M.W. Chen, T. Liu, X.B. Zhang, R.Q. Zhang, S. Tang, Y.H. Yuan, Z.J. Xie, Y.J. Liu, H. Wang, K.V. Fedorovich, N. Wang, Photoinduced Enhancement of Uranium Extraction from Seawater by MOF/Black Phosphorus Quantum Dots Heterojunction Anchored on Cellulose Nanofiber Aerogel, *Adv. Funct. Mater.* 31 (2021), 2100106.
- [43] F.T. Yu, Z.Q. Zhu, S.P. Wang, Y.K. Peng, Z.Z. Xu, Y. Tao, J.B. Xiong, Q.W. Fan, F. Luo, Tunable perylene-based donor-acceptor conjugated microporous polymer to significantly enhance photocatalytic uranium extraction from seawater, *Chem. Eng. J.* 412 (2021), 127558.
- [44] Y. Chen, M.J. Xu, J.Y. Wen, Y. Wan, Q.F. Zhao, X. Cao, Y. Ding, Z.L. Wang, H.X. Li, Z.F. Bian, Selective recovery of precious metals through photocatalysis, *Nat. Sustain.* 4 (2021) 618–626.
- [45] L. Yao, Y.Z. Hu, Y.T. Zou, Z.Y. Ji, S.X. Hu, C. Wang, P. Zhang, H. Yang, Z.W. Shen, D.Y. Tang, S. Zhang, G.X. Zhao, X.K. Wang, Selective and Efficient Photooxidation of Aqueous Cr(VI) as a Solid-State Polyhydroxy Cr(V) Complex for Environmental Remediation and Resource Recovery, *Environ. Sci. Technol.* (2022), <https://doi.org/10.1021/acs.est.2c03994>.
- [46] X.R. Li, Y. Chen, Y. Tao, L. Shen, Z.M. Xu, Z.F. Bian, H.X. Li, Challenges of photocatalysis and their coping strategies, *Chem. Catal.* 2 (2022) 1315–1345.
- [47] T. Chen, K. Yu, C. Dong, X. Yuan, X. Gong, J. Lian, X. Cao, M. Li, L. Zhou, B. Hu, R. He, W. Zhu, X. Wang, Advanced Photocatalysts for Uranium Extraction: Elaborate Design and Future Perspectives, *Coord. Chem. Rev.* 467 (2022), 214615.
- [48] Y.T. Song, A. Li, P.J. Li, L.W. He, D.Y. Xu, F.Q. Wu, F.W. Zhai, Y.T. Wu, K. Hu, S. A. Wang, M.V. Sheridan, Unassisted uranyl photoreduction and separation in a donor-acceptor covalent organic framework, *Chem. Mater.* 34 (2022) 2771–2778.
- [49] Z.J. Li, Z.W. Huang, W.L. Guo, L. Wang, L.R. Zheng, Z.F. Chai, W.Q. Shi, Enhanced Photocatalytic Removal of Uranium(VI) from Aqueous Solution by Magnetic TiO₂/Fe₃O₄ and Its Graphene Composite, *Environ. Sci. Technol.* 51 (2017) 5666–5674.
- [50] L.J. Feng, Y.H. Yuan, B.J. Yan, T.T. Feng, Y.P. Jian, J.C. Zhang, W.Y. Sun, K. Lin, G. S. Luo, N. Wang, Halogen hydrogen-bonded organic framework (XHOF) constructed by singlet open-shell diradical for efficient photoreduction of U(VI), *Nat. Commun.* 13 (2022) 1389.
- [51] P. Li, J.J. Wang, T. Peng, Y. Wang, J.J. Liang, D.Q. Pan, Q.H. Fan, Heterostructure of anatase-rutile aggregates boosting the photoreduction of U(VI), *Appl. Surf. Sci.* 483 (2019) 670–676.
- [52] J.J. Wang, Y. Wang, W. Wang, T. Peng, J.J. Liang, P. Li, D.Q. Pan, Q.H. Fan, W. S. Wu, Visible light driven Ti³⁺ self-doped TiO₂ for adsorption-photocatalysis of aqueous U(VI), *Environ. Pollut.* 262 (2020), 114373.
- [53] Z.M. Dong, Z.B. Zhang, Z.F. Li, Y. Feng, W.J. Dong, T. Wang, Z.P. Cheng, Y. Q. Wang, Y. Dai, X.H. Cao, Y.H. Liu, Y.H. Liu, 3D structure aerogels constructed by reduced graphene oxide and hollow TiO₂ spheres for efficient visible-light-driven photoreduction of U(VI) in air-equilibrated wastewater, *Environ. Sci. Nano* 8 (2021) 2372–2385.
- [54] X.H. Jiang, Q.J. Xing, X.B. Luo, F. Li, J.P. Zou, S.S. Liu, X. Li, X.K. Wang, Simultaneous photoreduction of Uranium(VI) and photooxidation of Arsenic(III) in aqueous solution over g-C₃N₄/TiO₂ heterostructured catalysts under simulated sunlight irradiation, *Appl. Catal. B: Environ.* 228 (2018) 29–38.
- [55] J.Y. Gong, Z.B. Xie, C.B. Xiong, C. Liu, Z.Q. Li, Z.G. Le, Efficient photocatalytic removal of U(VI) over π -electron-incorporated g-C₃N₄ under visible light irradiation, *J. Radioanal. Nucl. Chem.* 322 (2019) 1115–1125.
- [56] S.Y. Li, X.Y. Yang, Z.P. Cui, Y. Xu, Z.W. Niu, P. Li, D.P. Pan, W.S. Wu, Efficient photoreduction strategy for uranium immobilization based on graphite carbon nitride/perovskite oxide heterojunction nanocomposites, *Appl. Catal. B: Environ.* 298 (2021), 120625.
- [57] Z.R. Dai, S. Zhao, J.J. Lian, L. Li, D.X. Ding, Efficient visible-light-driven photoreduction of U(VI) by carbon dots modified porous g-C₃N₄, *Sep. Purif. Technol.* 298 (2022), 121590.
- [58] Z.R. Dai, Y.S. Sun, H. Zhang, D.X. Ding, L. Li, Photocatalytic reduction of U(VI) in aqueous solution by mGO/g-C₃N₄ nanocomposite under visible LED light irradiation, *Chemosphere* 254 (2020), 126671.
- [59] K.F. Yu, L. Tang, X. Cao, Z.H. Guo, Y. Zhang, N. Li, C.X. Dong, X. Gong, T. Chen, R. He, W.K. Zhu, Semiconducting Metal-Organic Frameworks Decorated with Spatially Separated Dual Cocatalysts for Efficient Uranium(VI) Photoreduction, *Adv. Funct. Mater.* 32 (2022), 2200315.
- [60] X. Zhong, Y.X. Liu, W.X. Zeng, Y.L. Zhu, B.W. Hu, Excellent photoreduction performance of U(VI) on metal organic framework/covalent organic framework heterojunction by solar-driven, *Sep. Purif. Technol.* 285 (2022), 120405.
- [61] Y. Zhang, H. Liu, F. Gao, X. Tan, Y. Cai, B. Hu, Q. Huang, M. Fang, X. Wang, Application of MOFs and COFs for photocatalysis in CO₂ reduction, H₂ generation, and environmental treatment, *EnergyChem* 4 (2022), 100078.
- [62] X. Liu, G. Verma, Z. Chen, B. Hu, Q. Huang, H. Yang, S. Ma, X. Wang, Metal-Organic Framework Nanocrystals Derived Hollow Porous Materials: Synthetic Strategies and Emerging Applications, *Innovation* 3 (2022), 100281.
- [63] X. Zhong, Y.X. Liu, S. Wang, Y.L. Zhu, B.W. Hu, In-situ growth of COF on BiOBr 2D material with excellent visible-light-responsive activity for U(VI) photocatalytic reduction, *Sep. Purif. Technol.* 279 (2021), 119627.
- [64] X. Liu, X. Wang, W. Jiang, C.R. Zhang, L. Zhang, R.P. Liang, J.D. Qiu, Covalent organic framework modified carbon nanotubes for removal of uranium (VI) from mining wastewater, *Chem. Eng. J.* 450 (2022), 138062.
- [65] S.J. Li, Y.Z. Hu, Z.W. Shen, Y.W. Cai, Z.Y. Ji, X.L. Tan, Z.X. Liu, G.X. Zhao, S.X. Hu, X.K. Wang, Rapid and selective uranium extraction from aqueous solution under visible light in the absence of solid photocatalyst, *Sci. China Chem.* 64 (2021) 1323–1331.
- [66] J. Kim, H. Kim, W.S. Kim, W. Um, Dissolution of studdite [UO₂(O₂)(H₂O)₄] in various geochemical conditions, *J. Environ. Radioact.* 189 (2018) 57–66.
- [67] F. Colmenero, L.J. Bonales, J. Cobos, V. Timon, Study of the thermal stability of studdite by in situ Raman spectroscopy and DFT calculations, *Spectrochim. Acta A Mol. Biomol. Spectrosc.* 174 (2017) 245–253.
- [68] T. Vitova, I. Pidchenko, S. Biswas, G. Beridze, P.W. Dunne, D. Schild, Z. Wang, P. M. Kowalski, R.J. Baker, Dehydration of the Uranyl Peroxide Studdite, [UO₂(η^2 -O₂)(H₂O)₂]-2H₂O, Affords a Drastic Change in the Electronic Structure: A Combined X-ray Spectroscopic and Theoretical Analysis, *Inorg. Chem.* 57 (2018) 1735–1743.
- [69] O. Spalek, J. Balej, I. Paseka, Kinetics of the decomposition of hydrogen peroxide in alkaline solutions, *J. Chem. Soc., Faraday Trans.* 78 (1982) 2349.
- [70] H.H. Wang, P. Mei, X.S. Huang, J.T. Xiao, Y.B. Sun, Uranyl(VI) boosting 3D g-C₃N₄ photocatalytic H₂O₂ production for U(VI) immobilization, *J. Clean. Prod.* 330 (2022), 129821.
- [71] N.B.A. Thompson, V.L. Frankland, J.W.G. Bright, D. Read, M.R. Gilbert, M. C. Stennett, N.C. Hyatt, The thermal decomposition of studdite: analysis of the amorphous phase, *J. Radioanal. Nucl. Ch* 327 (2021) 1335–1347.
- [72] H.D. Burrows, T.J. Kemp, The photochemistry of the uranyl ion, *Chem. Soc. Rev.* 3 (1974) 139–165.
- [73] M. Sarakha, M. Bolte, H.D. Burrows, Electron-transfer oxidation of chlorophenols by uranyl ion excited state in aqueous, *J. Phys. Chem. A* 104 (2000) 3142–3149.
- [74] R. Nagaishi, Y. Katsumura, K. Ishigure, H. Aoyagi, Z. Yoshida, T. Kimura, Y. Kato, Photoreduction of the uranyl ion in aqueous solution II. Alcohols in acid solutions, *J. Photochem. Photobiol. A* 146 (2002) 157–161.
- [75] K.F. Yu, P.Y. Jiang, H.B. Yuan, R. He, W.K. Zhu, L.B. Wang, Cu-based nanocrystals on ZnO for uranium photoreduction: Plasmon-assisted activity and entropy-driven stability, *Appl. Catal. B: Environ.* 288 (2021), 119978.
- [76] M.M. Hamilton, J.W. Ejniak, A.J. Carmichael, Uranium reactions with hydrogen peroxide studied by EPR-spin trapping with DMPO, *J. Chem. Soc., Perk. T. 2* (1997) 2491–2494.

- [77] S.J. Xie, Z.B. Shen, J. Deng, P. Guo, Q.H. Zhang, H.K. Zhang, C. Ma, Z. Jiang, J. Cheng, D.H. Deng, Y. Wang, Visible light-driven C-H activation and C-C coupling of methanol into ethylene glycol, *Nat. Commun.* 9 (2018) 1181.
- [78] W.D. Wang, A. Bakac, J.H. Espenson, Uranium(VI)-catalyzed photooxidation of hydrocarbons with molecular oxygen, *Inorg. Chem.* 34 (1995) 6034–6039.
- [79] Y. Li, J. Su, E. Mitchell, G.Q. Zhang, J. Li, Photocatalysis with visible-light-active uranyl complexes, *Sci. China Chem.* 56 (2013) 1671–1681.
- [80] V. Diesen, M. Jonsson, Formation of H₂O₂ in TiO₂ photocatalysis of oxygenated and deoxygenated aqueous systems: a probe for photocatalytically produced hydroxyl radicals, *J. Phys. Chem. C* 118 (2014) 10083–10087.